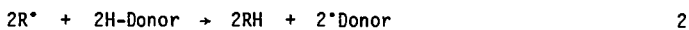


An Electron Spin Resonance Investigation of Free Radicals  
in Lignite Formed Using Programmed Temperatures,  $H_2S$ , CO and  $H_2$

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INTRODUCTION

The conversion of low-rank coal to liquid products has traditionally been performed in organic donor solvents at constant reactor temperatures. In one view of coal liquefaction, the thermolysis of weak bonds in the coal structure is followed by H transfer to the coal-derived radicals by hydrogenation atom donor molecules, reactions 1 and 2. To minimize addition and allow organic



materials to enter the product stream, we have recently developed a new donor solvent,  $H_2O$ - $H_2S$  with CO and  $H_2$ , as a substitute for the organic slurrying solvent (1,2) and reducing gases. For ZAP lignite, volatile product conversion for the reaction performed in  $H_2O$ - $H_2S$ - $H_2$ -CO at 420°C is 42.8%; and, for  $H_2O$ - $H_2$ -CO, it is 37.4% (1). Our current research into the chemistry of liquefaction has yielded considerable progress using the linear temperature programmed reactions, 300-500°C. The conversion to volatile products using by  $H_2O$ - $H_2S$ - $H_2$ -CO is equal 59.3% (3).

A number of investigators have applied ESR to examine radicals formed during pyrolysis of coal (4-11). Since the method of electron resonance is a very sensitive, we have chosen this technique to investigate mutual interactions of coal-derived radicals with reducing gases.

EXPERIMENTAL

The ZAP lignite (Table 1) was ground to less than 37  $\mu m$ . About 30-50 mg of lignite sample was inserted in a 2 mm i.d. Pyrex tube together with 20-30 mg of glass wool. The samples were dried in vacuum 1 Torr at 50°C for 3 hrs. The liquefaction was performed under reducing gases using the linear programmed temperature range of 300-500°C over the period of 1 hr in the batch autoclaves.

When the temperature 500°C was reached, the reactors were vented to remove oil and gas, cooled down in water (20°C) and next in ice.. The samples were immediately sealed under argon, and the ESR measurements were carried out within 10-15 min at room temperature. According to Petrakis (12), upon cooling to room temperature, spin concentrations in coal are, in general, the same as at the high temperature. The spin concentrations and g values were determined by the sample interchange method. DPPH was employed as the standard. Spin concentrations were calculated on final and initial amounts of lignite. The spin concentration (SC) data was employed to calculate the conversion to distillate products by using the equation 3. The calculated conversion (SC)

$$\% \text{ conversion (SC)} = \frac{\text{SC}(\text{final}) - \text{SC}(\text{initial})}{\text{SC}(\text{final})} \times 100\% \quad \underline{3}$$

has been correlated with similar conversion values into volatile products independently determined by employing the traditional techniques (1).

All ESR spectra were recorded using a Bruker ER-420 spectrometer. Duplicate samples were prepared for all different sets of liquefaction conditions to check reproducibility.

#### RESULTS AND DISCUSSION

##### (a) The effect of H<sub>2</sub>S on stabilization of coal-derived radicals

The typical ESR spectrum of a ZAP lignite sample is a single symmetric signal without hyperfine structure (Figure 1). This signal is distinguishable by its g-value, linewidth and spins g<sup>-1</sup>. For unreacted coal, they are 2.0021, 8.3 G and 1.8 x 10<sup>19</sup> spins g<sup>-1</sup>, and for pyrolyzed coal linear programmed over 300-500°C for 1 hr, the values are 2.0011, 6.8 G and 20.2 ± 1.9 x 10<sup>19</sup> g spins g<sup>-1</sup>, respectively. Decreases in ESR g value is known to be a consequence of the evolution of heteroatom-containing gases such as CO<sub>2</sub> and H<sub>2</sub>O which are formed during the pyrolyses (13). The decrease in linewidth of the sample can be attributed to the dehydrogenation reactions known to be occurring concurrently.

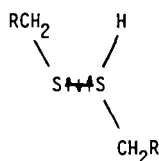
A representative spectrum of ZAP lignite which has been reacted with H<sub>2</sub>S is reproduced in Figure 2. This spectrum consists of two symmetric signals:

one is positive (+) and one is negative (-). The positive signal can be attributed to coal-derived and some organo-sulfur radicals. It is close to Lorentzian in shape. The observed negative curve has a Gaussian shape, and it represents radicals associated a variety of, organo-sulfur bonds. The existence of the negative signal suggests an altered magnetic environment of these unpaired electrons.

More recent measurements of the  $^{33}\text{S}$  hyperfine structure have revealed three basic forms of sulfide radicals:  $\text{RCH}_2\text{S}^\bullet$ ,  $\text{RCH}_2\text{SS}^\bullet$  and  $(\text{RCH}_2\text{SSCH}_2)^\bullet$  (14). The g tensor, which has proven to be widely applicable for identification of sulfur-centered radicals, does not provide a critical distinction between the monosulfide and disulfide forms of these radicals. There seems to be agreement (15) that the disulfide radical anion forms from  $\text{RS}^\bullet$  by reaction 4. The



unpaired electron is weakly bounded to the  $\text{S}\ddot{\text{S}}\sigma_{3p}^*$  antibonding molecular orbital since it contains a major  $3p+3p$  element. The disulfide radical anions can be protonated (16) to give I.



I

This molecule still has the unpaired electron in the  $\text{S}\ddot{\text{S}}\sigma_{3p}^*$  orbital. The S-S bond will probably be weaker than that of the anion.

In this system, one can expect the diffusion of  $\text{H}_2\text{S}$  inward in the coal particle during the heating. This may cause production several kinds of organo-sulfur bonds which can vary with different concentration of  $\text{H}_2\text{S}$ . It is reasonable to assume that charged organo-disulfide radicals can be also formed

in the interior of coal's grain and be distributed as paramagnetic impurities partly stabilized by environment.

By computer analysis of the spectra, it was possible to separate experimental ESR curve into two component spectra. The positive one belongs primarily to coal-derived radicals (positive) and the other to organo-disulfur radicals.

The relationship of spin concentrations per gram to the pressure of  $H_2S$  is shown in Figure 3. The lines assigned as I and II were determined by the division of the spin concentration values by the amount of charged lignite and recovered solid material from the reactor, respectively. There is a significant rise of spin density with increasing concentrations of  $H_2S$ . The differences in spin concentrations between the two plots I and II represents the amount of coal-derived radicals which have been converted to oil and gas. The line described as theoretical has been calculated from the computer separated signals, and represents the total number of radicals.

The variation of g-value with pressure of  $H_2S$  is presented in Figure 4. The g values increase significantly with  $H_2S$  pressure. It is related to the amount of heteroatoms incorporated (23). Thiophenolic forms like phenolic forms are effective at causing g-shifts (11).

Figure 5 shows the variation of the ESR line width ( $\Delta H_{pp}$ ) as a function of  $H_2S$  pressure. Overall the principal contributor to the positive signal is coal-derived radicals,  $\Delta H_{pp} \approx 5$  G and for signal (-) some kind of organo-disulfur compounds  $\Delta H_{pp} > 15$  G. The results indicate that hydrogen content in the coal radicals is unchanged with pressure of  $H_2S$ . For organo-disulfur compounds, the linewidths fall within the range 14.1-16.6 G with increasing of  $H_2S$  pressure. This suggests that other effects may also influence on the ESR linewidth such as electron-proton interactions (13).

It is worthwhile to note that negative ESR signal disappears when previously sulfurized ZAP lignite is exposed to  $H_2$  or CO atmospheres at 500°C. The g-values and linewidths concomitantly decrease to 2.0016 and 5.8 G, respectively.

(b) Effect of  $H_2S$  and  $H_2$  (CO) on hydrogenation of coal-derived radicals.

In  $H_2S-H_2$  or  $H_2S-CO$  atmospheres significant differences occur in ESR spectra of ZAP lignite programmed 300-500°C (Figure 6). The line shape varies and is characterized by the disappearance of the negative signal (Figure 2) and the appearance of a narrow peak with a short width of line  $\sim 1$  G. The spin concentration in  $H_2S-CO$  atmosphere is lower than in  $H_2S-H_2$  (Figure 7). Therefore, CO decreases the probability of the carbon sulfur bonds formation.

The g values of the ZAP lignite in  $H_2S-CO$  also changes upon the introduction of  $H_2$  particularly at lower pressures of  $H_2S$  (Figure 8). In the higher fractional pressure of CO ( $\approx 0.7$ ) in the mixture of  $H_2S + CO$  there appears, first of all, to be CO interaction with coal radicals. This is mostly pronounced in reaction CO alone with coal radicals (Table 1),  $g = 2.0026$  and suggest strong spin-orbit coupling, probably with phenoxy groups or those of the semiquinone type.

(c) Effect of water on free radicals formation and lignite conversion.

The results of the ESR measurements with water and reactant gases ( $CO$ ,  $H_2S$ ,  $H_2$ ) are listed in Table 1. In all experiments with  $H_2O$ , the radical concentrations of ZAP lignite is low considering the very large numbers of radicals known to be formed during pyrolysis ( $\approx 20.2 \times 10^{19} \text{ g}^{-1}$ ). The determined conversion to volatile products is varied with different pressure of CO. The maximum conversion was achieved mostly in  $CO = 70 \text{ MPa} + H_2S = 17.5 \text{ MPa}$ . This suggests that many of formed radicals were consumed by hydrogen transfer from shift reaction,  $H_2O + CO$ , shift reaction promoted by  $H_2S$  throughout COS intermediate compounds and as oil extracted by supercritical water or partly evaporated to reactor were removed during ventilation process. The very narrow linewidth was noted for reactions performed with  $H_2O$  and reactant gases. Using the relation between ESR spectral linewidth and hydrogen content of coals developed by Retcofsky (29),  $\Delta H_{pp} = 1.6 H - 1.8$  where H is weight percent hydrogen, we can conclude that the hydrogen content in the nonvolatile residue is decreased.

#### SUMMARY

To increase the liquid yields of coal liquefaction, ESR spectra of unconverted coal residues are related to reactor conditions and conversion into volatile products. ESR spectra were obtained for North Dakota Zap lignite treated with various reducing gas atmospheres using a linear-programmed reactor temperature range of 300-500°C. The line shape, spin density, linewidth and g-values were all found to vary with the nature of the reducing gases employed. The spin density of the coal samples increased with increasing concentrations of  $H_2S$  in the reactor. Partially superimposed positive and negative signals were recorded when the coal was reacted with  $H_2S$  alone. When  $H_2S$  is used in conjunction with either  $H_2$  or  $CO$ , only two positive signals were observed in the ESR spectra and the spin densities were reduced. The spin density of the reacted coal was minimum when the reaction mixture contained  $H_2O$ . The spin density of the samples were inversely related to the percent conversion into volatile products.

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Table 1. ESR Spectral Data and Distillate Conversion Results for ZAP Lignite.<sup>1</sup>

Pressure of gases (MPa)	g value	Linewidth (G)	Spin Density ( $\times 10^{19}$ ) $\frac{\text{spins g}^{-1}}{(\text{initial})}$	Conversion (SC) %	Distillate Conversion %
Pyrolysis <sup>2</sup>					
H <sub>2</sub> = 34.4	2.0011	6.8	20.2 $\pm$ 1.9	NA	NA
CO = 34.4	2.0016	6.3	6.1 $\pm$ 0.3	39.0	NA
H <sub>2</sub> , CO = 34.4	2.0026	10.6	11.7 $\pm$ 0.9	37.4	NA
	2.0026	6.3	4.0 $\pm$ 0.5	45.2	45.0
H <sub>2</sub> S = 17.5	2.0035	two signals (+,-)	34.2 $\pm$ 3.0	24.0	20.0
H <sub>2</sub> S = 17.5, CO = 34.4	2.0025	6.0	6.3 $\pm$ 0.7	39.4	39.8
H <sub>2</sub> S = 17.5; H <sub>2</sub> , CO = 34.4	2.0012	two signals (+,+)	2.8 $\pm$ 1.8	54.8	47.8
CO = 34.4; H <sub>2</sub> O = 0.8 g	2.0017	6.2	3.8 $\pm$ 1.2	42.4	43.8
CO = 70; H <sub>2</sub> O = 0.8 g	2.0016	4.4	1.3 $\pm$ 0.2	59.4	60.9
CO = 70; H <sub>2</sub> O = 0.8 g; H <sub>2</sub> S = 17.5	2.0018	2.2	0.5 $\pm$ 0.09	77.6	78.1
H <sub>2</sub> S = 17.5; H <sub>2</sub> , CO = 34.4; H <sub>2</sub> O = 0.8 g	2.0011	3.9	1.6 $\pm$ 0.4	57.9	59.9
H <sub>2</sub> S = 17.5; H <sub>2</sub> O = 0.8 g	2.0021	two signals (+,-)	19.2 $\pm$ 1.9	23.8	22.0
S/lignite = 0.94 <sup>2,3</sup>	2.0036	6.25	11.9	NA	NA
S/lignite = 0.33 <sup>2,3</sup>	2.0036	two signals (+,-)	24.7	NA	NA

<sup>1</sup>Experimental conditions for liquefaction, water = 0.8 g, pressure of gases are listed in the Table, reaction

temperature, 300-500°C, reaction time 1 hr, ventilation at 500°C.

<sup>2</sup>Reactions have been performed in sealed capillary tubes with no charged gases.

<sup>3</sup>Weight ratio of sulfur to lignite.



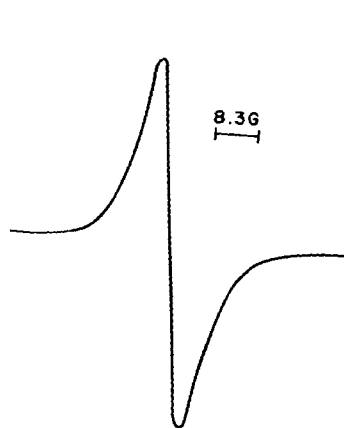


Figure 1. ESR spectrum of ZAP lignite.

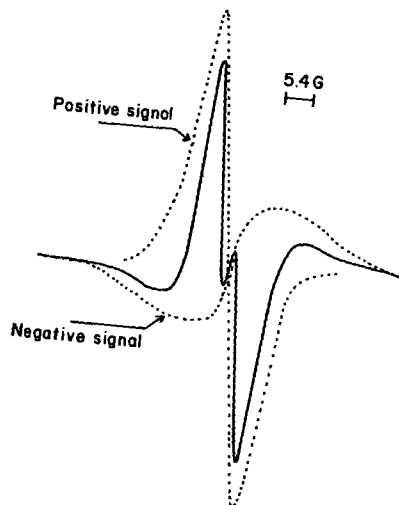


Figure 2. ESR spectrum of ZAP lignite after reaction with  $H_2S$ .

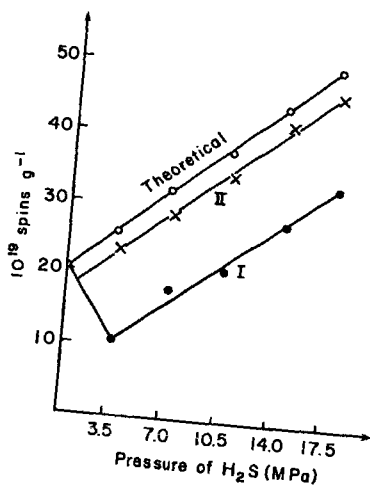


Figure 3. Variation of total radical concentration with pressure of  $H_2S$ .

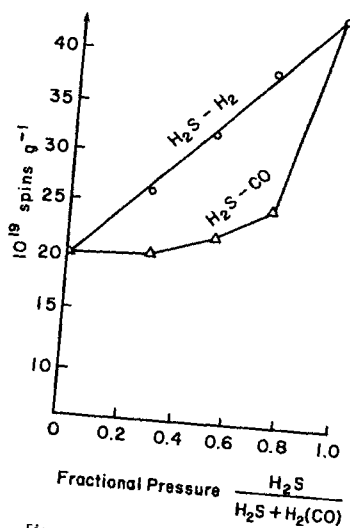


Figure 4. ESR g-value of ZAP lignite after reaction with  $H_2S$  at linear programmed temperature, 300-500°C.

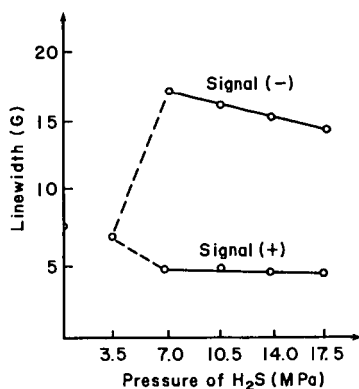


Figure 5. Variation of ESR spectral linewidth for recorded positive (+) and negative (-) signals with pressure of  $H_2S$ .

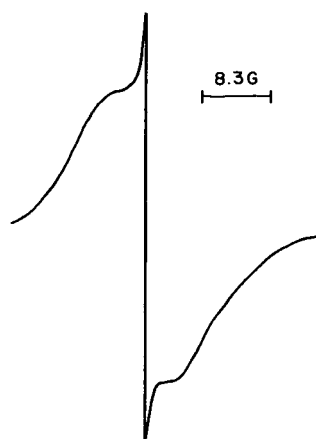


Figure 6. ESR spectrum of ZAP lignite after reaction with  $H_2S-H_2$  at linear programmed temperature, 300-500°C.

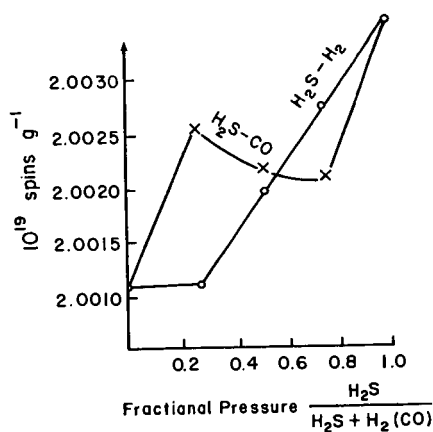


Figure 7. Variation of spin concentration with fractional pressure of  $H_2S$ .

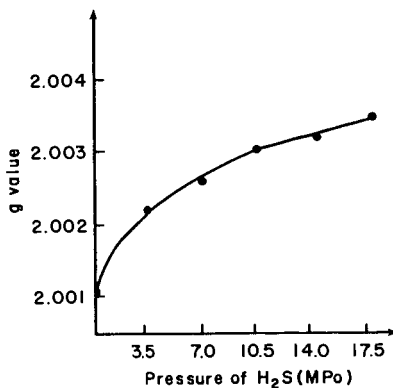


Figure 8. ESR g value of ZAP lignite versus fractional pressure of  $H_2S$ .